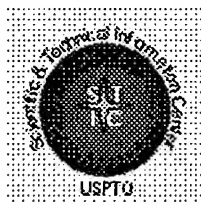


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Matthew T Canning, David A Brown, Daniel B Yarosh. *Photochemistry and Photobiology*. Augusta:
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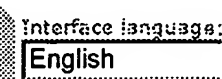
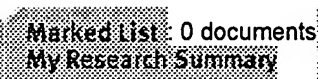
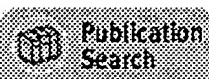
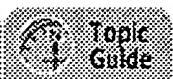
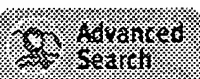
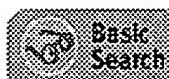
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An effective entry into the 3,4,7-metheno-3H-cyclopenta a pentalene (bisesquinane) ring system was achieved via a novel tandem alkylation-intramolecular 4 + 2 cycloaddition reaction. The addition of TMS-cyclopentadiene to 5,5-dimethoxynorbornene in the presence of Lewis acid catalysts produced 3b-methoxy-3a,3b,4,6a,7,7a-octahydro-3,4,7-metheno-3H-cyclopenta a pentalene (methoxybisesquinene) as the major product in addition to other C(13)H(16)O polycyclo-alkene isomers. A mechanism to account for the isomeric products requires rearrangements via (pi)-bond bridging to an intermediate allyl silane cation. A simple purification scheme via a bromination/debromination procedure was developed, thus affording methoxybisesquinene in high purity in an overall three-step process.

Addition reactions to methoxybisesquinene were quite facile and under kinetic conditions gave predominantly exo addition products without rearrangement. Under equilibrating conditions, Wagner-Meerwein skeletal rearrangements occurred to produce predominantly 2,4,7-metheno-3H-cyclopenta a pentalenes (twist-methoxybisesquinenes). In no case was further rearrangement observed to produce 11-keto-tetracyclo 6.2.1.1 ('3,6).0('2,7) -dodec-4-ene, the expected frangomeric cleavage product of the intermediate twist-methoxybisesquinane cation. In fact, under acidic conditions, this ketone was found to undergo homoconjugate addition to produce a twist-bisesquinane diol.

The unusual chemistry of the bisesquinane system can be accounted for by strain effects. Strain energies were calculated (MM2) for bisesquinane and related systems to probe the effect of strain on structure, bonding and reactivity. The calculated structural parameters for bisesquinane are compared with those obtained from an x-ray crystal structure of dibromomethoxybisesquinane. The two central bonds C(10,11) and C(5,12) are substantially longer than normal, implying that these bonds are stretched as a consequence of strain. As predicted on the basis of strain relief, homoketonization of bisesquinol produced a single ketone. The highly compressed bridgehead bond angles of bisesquinane contribute significantly to the strain energy and result in somewhat larger J(C-H) coupling constants than related bicyclo-alkenes. The structure of bisesquinane is unique compared to norbornane in that the bridge methylenes are "tied back" by the central C(10)-C(11) bond, which results in a much more open exo-face. The effects of these structural perturbations and strain on the stereochemistry of Diels-Alder reactions with dimethoxytetrachloro-cyclopentadiene and tetracyclone were investigated.

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- ☐ 2. **Part I. First generation design, synthesis, and evaluation of azepine-based cryptophycin analogues. Part II. Studies toward the total synthesis of (+)-nodulisporic acid A**
by Cho, Young Shin, Ph.D., University of Pennsylvania, 2002, 543 pages; AAT 3072983
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- ☐ 3. **Complex cyclooctanes from simple 2-pyridone mixtures: Photo[4+4]-cycloaddition and exploratory transformations.**
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- ☐ 4. **Investigation of the stereochemistry of the methyl-to-methylene elimination in the biosynthesis of several terpenes through the use of chiral methyl labeled compounds.**
by Elmore, Charles Sherman, Ph.D., University of Illinois at Urbana-Champaign, 1997, 171 pages; AAT 9812580
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- ☐ 5. **Occupational exposure to terpenes in saw mills and joinery shops.**
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- ☐ 6. **Chemical brown stain of Douglas-fir wood.**
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- ☐ 7. **cis-arenediols as versatile chiral synthons in the synthesis of prostaglandins, cyclitols, carbohydrates, and alkaloids.**
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- ☐ 8. **Synthesis of hydrophenanthrene natural products: Dehydroabietic acid as a synthon.**
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- ☐ 9. **STUDIES ON PINACOL CHEMISTRY.**
by BRUSS, DAN R., Ph.D., Montana State University, 1985, 137 pages; AAT 8528049

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- ☐ 2. **THE METABOLISM OF CYCLOALKANES BY DIFFERENT SPECIES OF XANTHOBACTER.**
by WARBURTON, ELIZABETH JEAN, Ph.D., Council for National Academic Awards (United Kingdom), 1989, 253 pages; AAT DX88842

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- ☐ 3. **SOLVOLYSES OF METHYL SUBSTITUTED BICYCLIC TERPENES.**
by CAMERON, PENELOPE JACKSON, Ph.D., University of California, Santa Barbara, 1967, 268 pages; AAT 6901716

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- ☐ 4. **REARRANGEMENTS OF THE BICYCLIC TERPENES**
by WILSON, JOSEPH D. C., II, Ph.D., The Pennsylvania State University, 1945, 87 pages; AAT 0000787

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- ☐ 2. **A bicyclic monoterpene diol and UVB stimulate BRCA1 phosphorylation in human keratinocytes**
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- Use "AND" to connect two words that don't need to be searched as a phrase.
- Connect similar terms with the "OR" operator (e.g. military OR pentagon). See [Search Tips](#) for more hints.

Basic Search

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